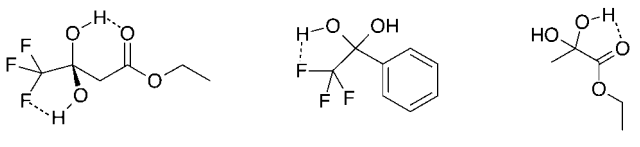

95 % 7 % 1 %

Scheme 3. Possible structures and the equilibrium fractions of the hydrates formed from different activated ketones. Values were measured by NMR spectroscopy in [D_8]THF containing 0.8 vol% water (water/reactant = 1.2:1).

modified Pt. Nevertheless, the frequently observed significant loss of *ee* with conversion of ethyl pyruvate in the best solvent AcOH (e.g. ref. [15]) may partly be attributed to the competing hydrogenolysis of the hydrate form, as this solvent generally has not been dried before use.

Experimental Section

Ethyl 4,4,4-trifluoroacetoacetate (**1;** Fluka, purum) was distilled before use, THF was dried over Na, and TFA was used as received. MeOCD was synthesized as described.[16] The 5 wt% Pt/Al_2O_3 catalyst (Engelhard 4759) was reduced in flowing hydrogen for 90 min at 400 °C before use.

The reactions were carried out at room temperature in an autoclave equipped with a 50 mL glass inlet and a PTFE cover. Prereduced catalyst (110 ± 3 mg) was added to a mixture of MeOCD (5.3 mg, 17.2 μmol) and reactant (0.34 g, 1.85 mmol) in 5 mL solvent. Water (40 μL; 0.8 vol%) was added either directly (6 min) or 15 h before the start of the reaction (preequilibration). Yields (Y) and *ee* values were dermined by direct gas chromatographic analysis of the reaction mixture using diglyme as an internal standard. The incremental *ee* was calculated as $\Delta ee = (ee_1 Y_1 - ee_2 Y_2)/(Y_2 - Y_1)$, where Y indicates yield to **2**, and index 2 refers to a sample taken subsequent to sample 1. Compounds **1a**, **1b**, and **3** were identified by ^{1}H, ^{13}C, and ^{19}F NMR spectroscopy.[17] Relative amounts of the different compounds were calculated by integration of the peak areas in the ^{19}F NMR spectra.

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The Mechanism of the [Cp_2TiMe_2]-Catalyzed Intermolecular Hydroamination of Alkynes**

Frauke Pohlki and Sven Doye*

The addition of ammonia or primary and secondary amines to nonactivated alkenes and alkynes is a direct and efficient approach towards the synthesis of higher substituted nitrogen-containing products. Although this hydroamination reaction is extremely interesting for industrial applications, efforts to develop related processes have met with only limited success.[1]

Inspired by the work of Bergman et al.[2a,b] and Livinghouse et al.,[2c–f] we recently reported that [Cp_2TiMe_2][3] is a very efficient catalyst for the intermolecular hydroamination of alkynes.[4] By using [Cp_2TiMe_2] as the catalyst, primary arylamines as well as sterically hindered *tert*-alkyl- and *sec*-alkylamines can be coupled to alkynes in high yields. However, hydroamination reactions employing sterically less hindered amines such as benzylamine or *n*-hexylamine are very slow and the corresponding products could only be isolated in poor yields. To explain the mentioned differences in the behavior of different amines and to understand the mechanistic details of the reaction a kinetic investigation was carried out.

Initial studies showed that the reaction between 1-phenylpropyne (**1**) and 4-methylaniline (**2**) is suitable for kinetic experiments (Scheme 1). In the presence of ferrocene as internal standard, the changes in the concentrations of **1**, **2**, and **3** (two isomers) could be determined by ^{1}H NMR spectroscopy.[5] Representative plots of $c(\mathbf{1})\,c_0(\mathbf{1})^{-1}$ versus time t for different concentrations of [Cp_2TiMe_2] are shown in Figure 1.

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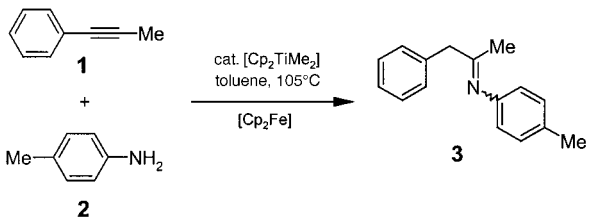
Supporting information for this article is available on the WWW under http://www.angewandte.com or from the author.



Scheme 1. Kinetically investigated reaction of 1-phenylpropyne (**1**) and 4-methylaniline (**2**).

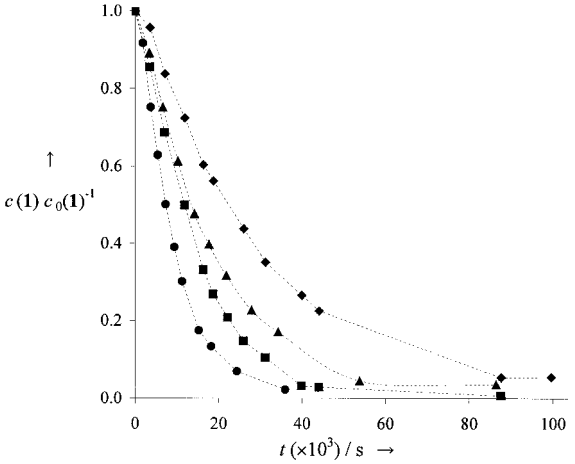


Figure 1. Representative plots of $c(\mathbf{1})c_0(\mathbf{1})^{-1}$ versus t for $[Cp_2TiMe_2]$ concentrations of 22.4 (●), 9.5 (■), 7.1 (▲), and 3.3 mol% (◆).

After a short induction period in which $[Cp_2TiMe_2]$ is probably converted into the catalytically active species, all obtained plots showed a first-order disappearance of alkyne **1**. Plots of $-\ln[c(\mathbf{1})c_0(\mathbf{1})^{-1}]$ versus t gave straight lines for all employed catalyst concentrations indicating that the rate law in Equation (1) (v = reaction rate) describes the reaction in a correct manner.

$$v = -\frac{dc(\mathbf{1})}{dt} = k_{obs}c(\mathbf{1}) \quad (1)$$

The obtained data for k_{obs} for different concentrations of $[Cp_2TiMe_2]$ are summarized in Table 1 (entries 1–14). A plot of k_{obs} versus $c([Cp_2TiMe_2])$ (Figure 2) shows that the reaction is not first order in $[Cp_2TiMe_2]$.

In addition, the dependence of the amine concentration on the rate of the reaction was investigated by determining k_{obs} for different concentrations of amine **2**, while the $[Cp_2TiMe_2]$ concentration remained constant. The obtained data (Table 1, entries 7, 15–17) are presented graphically in Figure 3, which clearly shows k_{obs} is not independent from the concentration of amine **2**.[6]

All mentioned observations can be explained by the complex mathematical relationship between k_{obs}, $c([Cp_2TiMe_2])$ and $c(\mathbf{2})$ shown in Equation (2)[7] which is consistent with the catalytic cycle outlined in Scheme 2. Interestingly, this catalytic cycle includes a reversible dimerization of the catalytically active imido complex **4**[8] and a reversible addition of **2** to **4**. The hydroamination of **1** takes place by a reversible [2+2] cycloaddition between **1** and **4**, a

Table 1. Determined rate constants k_{obs} at 105 ± 0.1 °C.

Entry	Catalyst	x(cat.) [mol%]	c(cat.) [mol L^{-1}]	$c_0(\mathbf{1})$ [mol L^{-1}]	$c(\mathbf{2})$ [mol L^{-1}]	k_{obs} [s^{-1}]
1	$[Cp_2TiMe_2]$	1.4	3.77×10^{-3}	0.278	2.54	8.14×10^{-6}
2	$[Cp_2TiMe_2]$	1.4	3.81×10^{-3}	0.270	2.50	1.50×10^{-5}
3	$[Cp_2TiMe_2]$	1.8	5.10×10^{-3}	0.278	2.48	9.65×10^{-6}
4	$[Cp_2TiMe_2]$	2.7	7.43×10^{-3}	0.272	2.53	3.23×10^{-5}
5	$[Cp_2TiMe_2]$	3.3	9.01×10^{-3}	0.272	2.56	3.44×10^{-5}
6	$[Cp_2TiMe_2]$	3.7	9.80×10^{-3}	0.267	2.57	4.46×10^{-5}
7	$[Cp_2TiMe_2]$	4.5	1.23×10^{-2}	0.276	2.66	5.21×10^{-5}
8	$[Cp_2TiMe_2]$	7.1	1.90×10^{-2}	0.269	2.50	5.84×10^{-5}
9	$[Cp_2TiMe_2]$	8.0	2.15×10^{-2}	0.270	2.50	6.91×10^{-5}
10	$[Cp_2TiMe_2]$	9.5	2.49×10^{-2}	0.263	2.58	8.73×10^{-5}
11	$[Cp_2TiMe_2]$	10.2	2.66×10^{-2}	0.261	2.53	8.68×10^{-5}
12	$[Cp_2TiMe_2]$	11.9	3.25×10^{-2}	0.257	2.55	8.72×10^{-5}
13	$[Cp_2TiMe_2]$	16.4	4.19×10^{-2}	0.256	2.54	9.49×10^{-5}
14	$[Cp_2TiMe_2]$	22.4	5.79×10^{-2}	0.259	2.72	1.18×10^{-4}
15	$[Cp_2TiMe_2]$	5.7	1.34×10^{-2}	0.237	1.28	4.32×10^{-5}
16	$[Cp_2TiMe_2]$	4.6	1.24×10^{-2}	0.270	3.22	5.73×10^{-5}
17	$[Cp_2TiMe_2]$	4.3	1.18×10^{-2}	0.272	3.87	5.71×10^{-5}
18	**10**	5.8	1.63×10^{-2}	0.279	2.51	3.93×10^{-5}
19	**11**	6.2	1.71×10^{-2}	0.275	2.52	6.70×10^{-5}

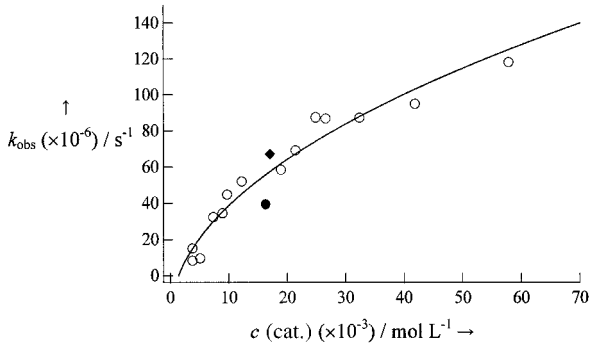


Figure 2. Plot of k_{obs} versus the $[Cp_2TiMe_2]$ concentration (○) with an additional fit-curve corresponding to Equation (3), as well as the k_{obs} data determined for **10** (●) and **11** (◆).

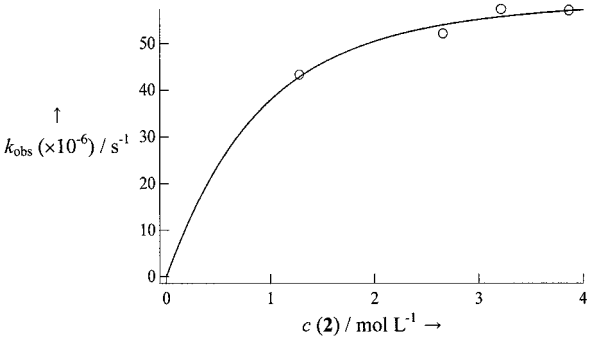


Figure 3. Plot of k_{obs} versus the concentration of amine **2** with an additional fit-curve corresponding to Equation (4).

protonation of the formed azametallacyclobutene **5**, and a final α-elimination of the product which regenerates **4**.

$$k_{obs} = -\frac{k_1k_2c(\mathbf{2})[K_2c(\mathbf{2})+1]}{4K_1[k_{-1}+k_2c(\mathbf{2})]} + \sqrt{\left(\frac{k_1k_2c(\mathbf{2})[K_2c(\mathbf{2})+1]}{4K_1[k_{-1}+k_2c(\mathbf{2})]}\right)^2 + \frac{k_1^2k_2^2c(\mathbf{2})^2}{2K_1[k_{-1}+k_2c(\mathbf{2})]^2}c([Cp_2TiMe_2])} \quad (2)$$

with $K_1 = \frac{c(\mathbf{8})}{c(\mathbf{4})^2}$ and $K_2 = \frac{c(\mathbf{9})}{c(\mathbf{2})c(\mathbf{4})}$

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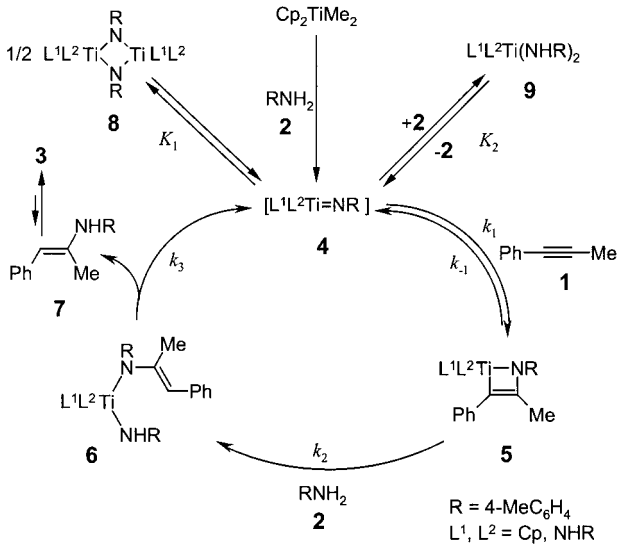

Scheme 2. Mechanism of the $[Cp_2TiMe_2]$-catalyzed hydroamination of 1-phenylpropyne (**1**) with 4-methylaniline (**2**).

First of all, Equation (2) predicts that large values for the equilibrium constants K_1 and K_2 result in small values for k_{obs} and therefore decreased reaction rates. Since K_1 and K_2 probably increase if sterically less demanding amines are used Equation (2) easily explains the poor reactivity of benzylamine and *n*-hexylamine observed in the past.[4a]

Since the concentration of the amine **2** was kept constant during the investigation of the relationship between k_{obs} and $c([Cp_2TiMe_2])$, Equation (2) can be simplified to Equation (3). The additional parameter p_3 was introduced to consider a possible decomposition of the catalyst caused by trace amounts of water on the glassware.

$$k_{obs} = -p_1 + \sqrt{p_1^2 + p_2 c([Cp_2TiMe_2])} + p_3 \quad (3)$$

A fit-curve corresponding to Equation (3), which was calculated and plotted (program Igor-Pro (Version 4)) for the obtained data, demonstrates that this equation explains the relationship between k_{obs} and $c([Cp_2TiMe_2])$ in a correct way (Figure 2).[9] In addition, for a constant concentration of $[Cp_2TiMe_2]$ Equation (2) can be simplified to Equation (4) if it is assumed that $K_2 c(\mathbf{2}) \gg 1$ and $k_{-1} \gg k_2 c(\mathbf{2})$; thus, Equation (4) describes the relationship between k_{obs} and $c(\mathbf{2})$.

$$k_{obs} = -p_4 c(\mathbf{2})^2 + \sqrt{p_4^2 c(\mathbf{2})^4 + p_5 c(\mathbf{2})^2} \quad (4)$$

In Figure 3 a fit-curve corresponding to Equation (4) is plotted for the obtained data for k_{obs};[10] it clearly shows that Equation (4) describes the relationship between k_{obs} and $c(\mathbf{2})$ in a correct way. The assumptions $K_2 c(\mathbf{2}) \gg 1$ and $k_{-1} \gg k_2 c(\mathbf{2})$, which were necessary to simplify Equation (2) to Equation (4), indicate that the equilibrium between the imido complex **4** and the bisamide **9** strongly favors the bisamide **9** and that the protonation of the azametallacyclobutene **5** is slow compared to the cycloreversion of **5**.

For a comparison of the catalytic activities of $[Cp_2TiMe_2]$ and the recently identified hydroamination catalysts $[Cp^*TiMe_3]$[11] (**10**) ($Cp^* = C_5Me_5$) and [CpTi=N*t*Bu(Cl)Py] (**11**),[12] k_{obs} values were determined for these complexes (Table 1, entries 18, 19).[13] It was found that at 105 °C **10** is slightly less active than $[Cp_2TiMe_2]$, while the catalytic activities of **11** and $[Cp_2TiMe_2]$ are almost the same (Figure 2). This similar catalytic activity suggests that under the reaction conditions the same catalytically active species is formed from $[Cp_2TiMe_2]$ and **11**.[8] Since no induction period was observed for reactions employing **11** as the catalyst, this conversion seems to be faster for **11**.[14] However, the obtained results for **10** and **11** undoubtly show that other easily accessible titanium complexes also catalyze the hydroamination of alkynes.[13]

In conclusion, the obtained kinetic data suggest that the mechanism of the $[Cp_2TiMe_2]$-catalyzed intermolecular hydroamination of alkynes is correctly described by Scheme 2. It is important that a reversible equilibrium exists between the catalytically active species **4** and the dimer **8**. This equilibrium is responsible for the fact that no linear relationship between the catalyst concentration and the observed rate of the reaction exists. Furthermore, the kinetic data are consistent with the assumption that the protonation of the azatitanacyclobutene **5** is slow compared to the cycloreversion of **5**. These relationships are thus opposite to those established by Bergman et al. for the hydroamination of allenes.[8b] In addition, the mechanism shown in Scheme 2 explains the fact that sterically demanding amines are better substrates for the $[Cp_2TiMe_2]$-catalyzed hydroamination of alkynes than sterically less hindered amines because the equilibria between imido complex, imido complex dimer, and bisamide for sterically hindered amines favor a fast reaction. Furthermore, it was shown that mono-Cp– and Cp*–titanium complexes are also active hydroamination catalysts.

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[5] The kinetic experiments were carried out with a tenfold excess of amine **2** at 105 ± 0.1 °C, and the concentration of alkyne **1** was monitored as a function of time by ^{1}H NMR spectroscopy. The reaction times were between 10 and 96 h. At 105 °C, corresponding reactions employing 2,6-dimethylaniline went to completion in less than 60 min.

[6] In addition, experiments were carried out with a tenfold excess of alkyne **1**, and the concentration of amine **2** was monitored as a

function of time by ^{1}H NMR spectroscopy. Since the observed rate decreased with decreasing amine concentration it was clear that k_{obs} decreases with decreasing amine concentration.

[7] The mathematical derivation of Equation (2) can be found in the Supporting Information.

[8] a) The kinetic experiments carried out in this work do not give any information about the ligands L^1 and L^2 remaining at the titanium center. b) A recently published study suggests that a cyclopentadienide ligand ($L^1 = Cp$) and an amide ligand ($L^2 = 4\text{-}MeC_6H_4NH$) are bound to the titanium center. J. S. Johnson, R. G. Bergman, *J. Am. Chem. Soc.* **2001**, *123*, 2923 – 2924.

[9] The calculated parameters for the coefficients in Equation (3) are: $p_1 = 8.4574 \times 10^{-7} \pm 0.00087\ s^{-1}$; $p_2 = (3.775 \pm 1.06) \times 10^{-7}\ L\,mol^{-1}\,s^{-2}$, $p_3 = -2.1873 \times 10^{-5} \pm 0.000849\ s^{-1}$.

[10] The calculated parameters for the coefficients in Equation (4) are: $p_4 = (3.1595 \pm 0.802) \times 10^{-5}\ L^2\,mol^{-2}\,s^{-1}$; $p_5 = (3.8245 \pm 0.871) \times 10^{-9}\ L^2\,mol^{-2}\,s^{-2}$.

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[13] Investigations dealing with the catalytic activity of $[CpTi(NHPh)_3]$, $[Cp_2Ti{=}NtBuPy]$ and $[Cp(Ph_3P{=}N)TiMe_2]$ which are also active hydroamination catalysts will be published in due course.

[14] This observation suggests that in accord with Bergman's observations[8b] a mono-Cp complex is the catalytically active species. For $[Cp_2TiMe_2]$-catalyzed reactions this species must be formed by a loss of CH_4 and an exchange of one Cp ligand during the induction period.

$E(SiMe_3)_4^+$ Ions (E = P, As): Persilylated Phosphonium and Arsonium Ions**

Matthias Driess,* Rainer Barmeyer, Christian Monsé, and Klaus Merz

Dedicated to Professor Bob West

It is known that increasing or even reversing (umpolung) the bond polarity in isoelectronic compounds greatly increases the synthetic utility of a functional group. With this in mind we have been interested in the existence of organometallic-substituted cations of the Group 15 elements, EM_4^+ (E = N, P, As, Sb, Bi; M = semimetal, metal), depending upon the nature and number of the bound metal atoms the structure and reactivity of these compounds could be very different from that of the classical parent compounds as well as from the analogous halogen and organo-substituted EX_4^+ ions (X = H, halogen, alkyl, aryl). Thus, phosphonium ions bound exclusively to organometallic groups can be regarded most simply as masked *anionic* P centers, enclosed within a protective positively charged shell, whereas the PX_4^+ ions, in which X = halogen, represent the opposite (umpolung) extreme and have masked, strongly *cationic* P centers surrounded by a halide shell. To date few completely organometallic-substituted onium ions of the Group 15 elements are known, these compounds however, have remarkable structures and reactivities. The tetragold- and the tetrazirconocenyl-substituted onium ions $E(AuPR_3)_4^+$ (E = N, P, As)[1] and $E[Zr(\eta^5\text{-}C_5H_5)_2H]_4^+$ (E = P, As)[2] are the only transition metal derivatives of the EH_4^+ ions (E = N, P, As) to be described so far and show striking electronic and geometric differences. Recently we reported the first main group metal substituted ammonium and phosphonium ions of the type $E(SnMe_3)_4^+$ (E = N, P), which can also be regarded as base-stabilized stannylium ions and are only stable in nonpolar solvents and in the presence of noncoordinating counterions.[3] They are formed with surprising ease by the stannylation of $E(SnMe_3)_3$ with Me_3SnOTf ($OTf = OSO_2CF_3$, triflate) in toluene. In contrast, the simple $E(SiMe_3)_4^+$ ions are not so accessible.[4] In addition, attempts to make the $P(SiMe_3)_4^+$ ions from $[Me_3Si\text{-}Co(CO)_4]$, as the silylation agent, and $P(SiMe_3)_3$ were not successful, although Me_3P, Me_2PSiMe_3, and $MeP(SiMe_3)_2$ could be converted by this method into the corresponding mono-, di-, and trisilylphosphonium ions.[5] The desired tetrasilylonium ions should therefore be accessible from the more electrophilic silylium salts $R_3Si^+X^-$ containing noncoordinating anions. The easily prepared arene solvates $[Me_3Si(L)^+B(C_6F_5)_4^-]$ (L = C_6H_6, $C_6H_5CH_3$) **1a**, **b**[6] do indeed react smoothly with $P(SiMe_3)_3$ in toluene to give the desired $P(SiMe_3)_4$ salt **2**, which was isolated in the form of

$$[Me_3Si(L)]^+X^- \xrightarrow[-\,L]{E(SiMe_3)_3} [(Me_3Si)_4E]^+X^-$$

1a: L = C_6H_6 **2**: E = P

1b: L = $C_6H_5CH_3$ **3**: E = As

X = $B(C_6F_5)_4$

colorless cubic crystals in 87 % yield. In contrast, $N(SiMe_3)_3$ is inert to **1a**, **b**, whereas the quarternization of the weakly basic $As(SiMe_3)_3$ takes place without problem, giving the colorless crystalline $As(SiMe_3)_4$ salt **3** in 78 % yield. Compound **3**, however, cannot be prepared from the toluene solvate **1b** for kinetic reasons because in the presence of toluene the arsonium salt **3** is as stable as the phosphonium salt **2**.

Compounds **2** and **3** are soluble in CH_2Cl_2 and do not dissociate in this solvent. The ^{1}H NMR spectrum of a highly dilute solution of **2** displays a doublet at $\delta = 0.64$ ($^3J(H,P) = 6.3$ Hz) arising from the $SiMe_3$ protons, this signal is temperature independent between -30 and $+30\,^\circ$C. The arsonium ion in **3** behaves similarly, and gives a singlet at $\delta = 0.58$. The ^{31}P NMR spectrum of **2** shows a sharp singlet at $\delta = -200.1$, thus indicating that the ^{31}P nucleus is approximately 50 ppm more deshielded than in $P(SiMe_3)_3$. The deshielding is almost identical to the $\Delta\delta$ values of the corresponding $Me_{3-n}P(SiMe_3)_n/[Me_{3-n}P(SiMe_3)_{n+1}]^+$ pair, however, the latter species does dissociate slightly in solution.[5] In addition a ^{75}As NMR

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